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Two New Dammarane Glycosides from the Acid Hydrolysis Product of *Panax Notoginseng*

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Abstracts: Two new dammarane glycosides named notoginsenoside T_1 and T_2 were isolated from the mild acid hydrolysis products of the root saponins of *Panax notoginseng*. On the basis of spectroscopic evidences, their structures were elucidated to be 6-O-β-D-glucopyranosyl-24(25)-epoxy-3β,6α,12β,23ξ-tetrahydroxydammar-20(22)(*E*)-ene **1** and 6-O-β-D-glucopyranosyl-24(25)-epoxy-23ξ-methoxyl-3β,6α,12β-trihydroxydamm-ar-20(22)(*E*)-ene **2**, respectively.

Keywords: *Panax notoginseng*, dammarane glycosides, notoginsenoside T_1, T_2.

In our continuing research works on *Panax notoginseng* (Burk.) F. H. Chen, a famous traditional Chinese herb medicine[1], two new dammarane glycosides named notoginsenosides T_1 (**1**) and T_2 (**2**) were isolated from the mild acid hydrolysis products of the root saponins. We report herein the structure elucidation of these two novel glycosides.

Notoginsenosides T_1(**1**) was obtained as white solid, $[\alpha]_D^{26}$ = +14.49 (0.50, MeOH). Its negative mode HR-FAB-MS spectrum showing the quasimolecular ion peak at *m/z* 651.4139 $[M-1]^-$indicated the molecular formula $C_{36}H_{60}O_{10}$ (calcd. 651.4108). ^1H and ^{13}C NMR spectra of **1** showed one anomeric proton signal at δ5.02 (H-1', d, 7.3Hz) and one anomeric carbon signal at δ 106.1 (C-1') respectively, suggesting of the presence of one sugar moiety. There were two olefinic carbon signals at δ143.1 and δ124.8. The ^1H and ^{13}C NMR spectra data of **1** were very similar with those of ginsenoside Rh_4 **3** isolated previously from the Korean red ginseng (*Panax ginseng*)[2] except the side chain of aglycone moiety. The fact that **1** has seven unsaturated degree calculated from the molecular formula as Rh_4 **3** but one double bond less, indicated the presence of one more cycle in the side chain of **1**. The side chain structure of **1** was identified by the information from H-H COSY and HMBC experiments. In the ^1H-^1H COSY of **1**, an oxymethine proton signal at δ 4.68 (dd, J = 8.0Hz, 9.6Hz, H-23) correlated to an olefinic proton at δ 5.89 (d, J = 9.6Hz, H-22) and an epoxy proton at δ 3.22 (d, J = 8.0Hz, H-24). Furthermore, HMBC showed correlation from following protons to carbons: δ_H 1.85 (s, H-21) correlated to δ_C 50.8 (C-17), 124.8 (C-22), 143.1 (C-20); δ_H5.89 (d, J = 9.6Hz, H-22) to δ_C 13.8 (C-21), 50.8 (C-17), 66.7 (C-24); δ_H 4.68 (dd, J = 8.0Hz, 9.6Hz, H-23) to δ_C 66.7 (C-24), 120.6 (C-22), 146.5 (C-20); δ_H 3.22 (d, J = 8.0Hz, H-24) to δ_C 57.3

(C-25), 78.0 (C-23); both δ_H 1.28 (s, H-26) and δ_H 1.48 (s, H-27) to δ_C 66.7 (C-24) and 57.3 (C-25) (**Figure 1**). The stereochemical conformation of the double bond was characterized to be (*E*) form on the basis of NOE correlation between following proton signals: δ 1.85 (s, H-21) and δ 4.68 (dd, J = 8.0Hz, 9.6Hz, H-23); δ 5.89 (d, J = 9.6Hz, H-22) and δ 2.81 (ddd, J = 6.1Hz, 6.7Hz, 10.6Hz, H-17), 3.22 (d, J = 8.0Hz, H-24) in the ROESY spectrum (**Figure 2**). This deduction was also confirmed by the chemical shift of C-21 methyl group (δ 13.8) compared with the reference[2-5]. From above evidences, the structure of glycoside **1** was established as 6-O-β-D-glucopyranosyl-24(25)-epoxy-3β, 6α,12β,23 ξ -tetrahydroxydammar-20(22) (*E*)-ene.

Figure 1 Key correlation of **1** from HMBC

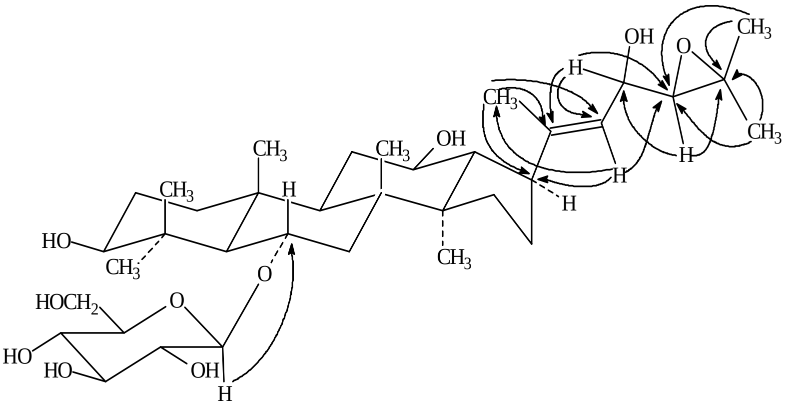
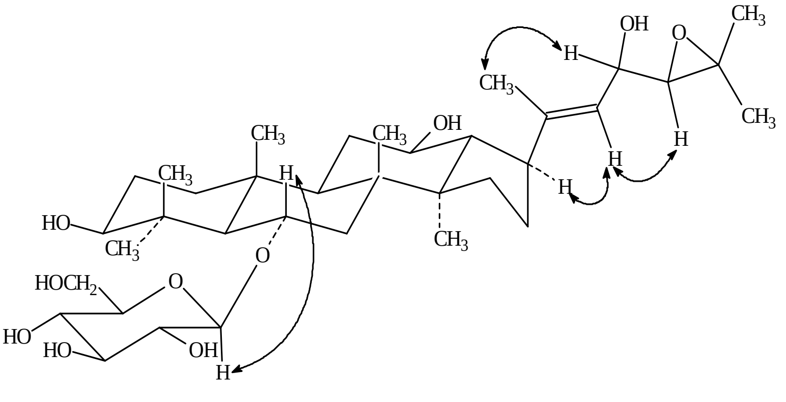
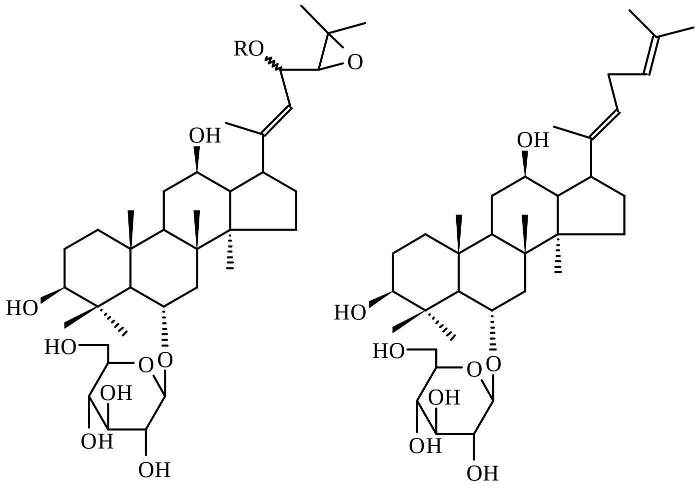


Figure 2 Key NOE correlation of **1** from ROESY





1. R=H **3**. Ginsenoside Rh_4

2. R=CH_3

Table 1 ^{13}C (125MHz) chemical shifts of notoginsenoside T_1 (**1**), T_2 (**2**) and ginsenoside Rh_4 (**3**) (δ in pyridine-d_5)

C	1	2	3	C	1	2	3
1	39.6	39.5	38.9	16	28.7	29.3	26.9
2	28.0	28.0	27.3	17	50.9	50.8a	50.1
3	78.6	78.6	79.5	18	17.8	17.8	17.2
4	40.4	40.4	39.8	19	17.4	17.4	17.2
5	61.5	61.5	60.9	20	143.1	146.5	139.5
6	80.1	80.1	78.0	21	13.8	14.1	12.5
7	45.5	45.4	44.7	22	124.8	120.6	122.9
8	41.4	41.4	40.8	23	68.8	78.0	29.4
9	50.8	50.8a	50.0	24	68.6	66.7	124.7
10	39.8	39.8	39.2	25	58.6	57.3	130.7
11	32.8	32.7	31.1	26	25.3	25.0	25.1
12	72.4	72.2	71.2	27	20.2	20.0	16.8
13	50.7	50.7	49.8	28	31.8	31.8	31.1
14	51.0	51.0	50.3	29	16.4	16.4	15.8
15	32.6	32.6	32.0	30	16.8	16.8	16.2
				OCH_3		55.6	
Glc 1’	106.1	106.1	105.4	4’	72.0	71.9	72.0
2’	75.5	75.5	74.8	5’	78.2	78.2	77.5
3’	79.7	79.7	79.0	6’	63.2	63.2	62.5

a: signals overlapped

Notoginsenoside T_2 (**2**) was obtained as white solid, $[\alpha]_D^{25}$ = +28.38 (0.41, MeOH). Its quasimolecular ion peak at *m/z* 665.4227 $[M-1]^-$ in the negative mode HR-FAB-MS spectrum revealed its molecular formula to be $C_{37}H_{62}O_{10}$ (calcd. 665.4265). The chemical shifts of the ^1H and ^{13}C NMR spectra of **2** closely resembled to those of **1** except those for the side chain of the aglycone moiety. Compared with **1**, glycoside **2** had one more methoxyl group whose carbon signal was at δ55.6 and proton signal at δ 3.42 (3H, s). Furthermore, the chemical shift of C-23 (δ 78.0) was downfield shifted by 9.2 ppm, C-22 (δ 120.6) and C-24 (δ 66.7) were upfield shifted by 4.2 and 1.9 ppm respectively. These findings suggested that the methoxyl group might be located at C-23 position. This deduction was confirmed by ^{1}H and ^{13}C long range correlation between the methoxyl proton (δ 3.42) and C-23 (δ 78.0) in HMBC spectrum. Thus, the structure of **2** was determined as 6-O-β-D-glucopyranosyl-24(25)-epoxy-23 ξ -methoxyl-3β,6α,12β-trihydroxydammar-20 (22)(*E*)-ene.

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